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Improved Routes towards Solution Deposition of Indium Sulfide Thin Films for Photovoltaic Applications:

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ABSTRACT

Conditions necessary for the reproducible deposition of pristine In_2S_3 thin films on TO-glass substrates by low temperature solution deposition have been identified. Baths containing carboxylic acids yield adherent, specular and crystalline films, within a defined pH range, dependent on the particular acid employed. Films have been characterised by XRD, SEM, XPS and electronic spectroscopy. As-deposited films were found to crystallise as tetragonal $\beta\text{-In}_2\text{S}_3$, no evidence for incorporation of hydroxy-indium species was found by XPS measurements.

INTRODUCTION

The III-VI semiconductor indium sulfide (In_2S_3) has been the focus of much attention during the past two decades, primarily due to its optoelectronic properties. The compound has inspired applications in the preparation of green and red phosphors [1] and more recently in semiconductor-sensitized solar cells [2]. Indium sulfide is an n-type semiconductor that exists in three forms, *viz.* a defect cubic structure $\alpha\text{-In}_2\text{S}_3$ under ambient conditions, which transforms into a defect spinel $\beta\text{-In}_2\text{S}_3$ at 693 K and into a layered structure $\gamma\text{-In}_2\text{S}_3$ at 1013 K [3-5]. The bandgap of In_2S_3 varies between 2.0 and 2.45 eV depending upon the composition [6].

An important research goal within the photovoltaic industry is the replacement of toxic heavy metals, such as cadmium, with more benign materials. The replacement of n-type CdS layers in polycrystalline heterojunction thin film solar cells employing CIS, CIGS or CdTe absorber layers, is of particular interest. Thin films of In_2S_3 have been demonstrated to be a suitable substitute for such layers in CIGS based cells. Films are most commonly deposited by the chemical bath method (CBD). Efficiencies of 15.7 % have been obtained for such devices, comparable to 16 % obtained for the standard CBD CdS buffer layer [7].

It is known that the composition, structure and morphology of CBD films are highly sensitive to deposition conditions (*e.g.* bath chemistry and nature of substrate surface). Such sensitivity grants the investigator the potential for tailoring the material properties of films by judicious selection of CBD conditions. Various groups have reported CBD- $\text{In}_x(\text{OH},\text{S})_y$ [7-9] but to date, no convincing studies have been presented for the CBD of pristine and crystalline In_2S_3 . The most satisfactory films have been deposited from baths containing acetic acid.

In preliminary studies, we have identified the conditions necessary for reproducible CBD- In_2S_3 on TO-glass from baths containing carboxylic acids. Our approach may offer a general route towards low temperature deposition of crystalline thin films of $\beta\text{-In}_2\text{S}_3$ with no hydroxide incorporation.

EXPERIMENTAL DETAILS

CBD of In_2S_3 thin films

Thin films of In_2S_3 were deposited on commercial TO glass substrates (Hartford Glass, USA) immersed in baths containing InCl_3 ($0.0083 \text{ mol dm}^{-3}$), a carboxylic acid CA (0.1 mol dm^{-3}) and thioacetamide (0.1 mol dm^{-3}). A standard procedure was adopted for the cleaning of the substrates prior to the CBD process in order to achieve reproducible results. Based on results obtained from preliminary experiments, which were performed with no pH adjustment, a range of optimal CBD conditions were identified for each CA for the deposition of adherent and specular films. Subsequent work involved optimisation of each CA-based CBD system within the defined pH range. Bath conditions are given in Table 1. The pH of the final solution was adjusted accordingly by the dropwise addition of NaOH or HCl (5 mol dm^{-3}). A Mettler Toledo MA 235 pH/ ion analyser and InLab 413 electrode were used to record solution pH. The temperature of the solution was maintained at 80°C for a total deposition time of 30 minutes. Films were annealed for 30 min at 400°C under a dynamic flow of argon.

Characterisation of thin films

X-ray diffraction studies were performed using secondary graphite monochromated $\text{Cu K}\alpha$ radiation (40 kV) on a Philips X'Pert Materials Diffractometer (MPD). Measurements were taken using a glancing angle incidence detector at an angle of 3° for 2θ values over $10-95^\circ$ in steps of 0.04 with a count time of 2 s. Scanning electron microscopy of Au coated samples was carried out on a Philips 525 SEM instrument. The XPS measurements were performed in the ultra-high vacuum chamber (base pressure of 10^{-8} Pa) of a Kratos ES 200 spectrometer using Mg $\text{K}\alpha$ excitation (analyser pass energy of 65 eV). The energy scale was calibrated using Au and Ag as a reference. Electronic absorption spectra were obtained with a He λ ios Beta Thermospectronic spectrophotometer. For direct bandgap semiconductors, extrapolation of the linear region of plots of α^2 versus $h\nu$ allows determination of the optical bandgap.

RESULTS AND DISCUSSION

The pattern of results for each of the CA-based CBD systems in the present study was very similar. Films deposited from baths of pH values lower than the optimal range were orange, matt but adherent. Films formed in the optimal pH range were yellow, specular and adherent whereas at higher pH values, only white hydroxy-indium films were deposited. The induction period (T^*) for growth of films (*i.e.* the interval between the point the bath reaches the requisite temperature and the appearance of visible colloidal material) was inversely related to $\text{pK}_{\text{a}1}$ of the acid. For example, baths at pH = 2 containing citric acid ($\text{pK}_{\text{a}1}$ 3.13) had T^* values ~ 7 min, baths containing acetic acid ($\text{pK}_{\text{a}1}$ 4.75) had T^* values ~ 2 min. The observation could be rationalised in terms of the speciation of the carboxylate-indium species for each CA, which acts to buffer the free indium concentration to low levels in solution. The speciation studies will be reported in more detail in a future paper.

Table I. Carboxylic acids used in CBD of In_2S_3 .

Carboxylic acid	pK_{a1} Values	Unadjusted bath pH	pH range	Optimal pH range
citric acid	3.13	1.95	1.50 – 2.20	1.95 – 2.10
formic acid	3.75	2.20	1.00 – 3.00	2.00 – 2.20
succinic acid	4.19	2.30	1.60 – 2.50	2.10 – 2.35
acetic acid	4.75	2.49	1.60 – 2.60	2.10 – 2.30

X-ray diffraction

X-ray diffraction patterns obtained for CBD In_2S_3 thin films deposited on TO glass in this study indicate that films are highly crystalline. Annealing of films (400°C under Ar) produced a colour change (yellow to pale orange for specular films, orange to light brown for matt films) and a slight enhancement in crystallinity. No significant differences were evident in XRD traces from films obtained from baths containing different carboxylic acids, within the effective pH ranges. Films were indexed to tetragonal $\beta\text{-In}_2\text{S}_3$ (JCPDS 25-0390). The lack of diagnostic reflections in the region $2\theta \sim 90\text{--}130^\circ$ was taken as evidence for the absence of $\alpha\text{-In}_2\text{S}_3$ modification. Discernible differences in preferred orientation were apparent for films grown within and lower than the optimal pH range from baths containing a given carboxylic acid. For example, films deposited from baths containing formic acid at lower pH showed preferred orientation in the (109) direction; thin specular films deposited in the optimal pH range grew preferentially along the (211) direction (see Figure 1).

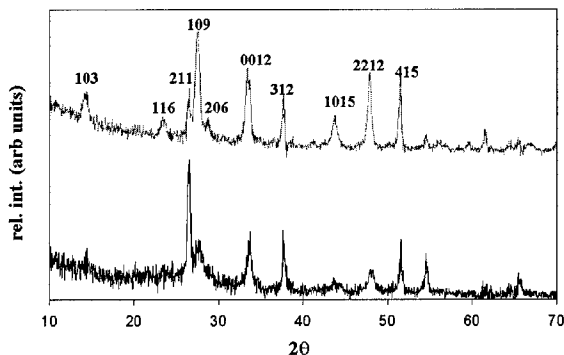


Figure1. XRD pattern of In_2S_3 thin films deposited from baths containing InCl_3 , formic acid and thioacetamide at pH 2.2 (bottom) and 1.4 (top). Films indexed to $\beta\text{-In}_2\text{S}_3$ (JCPDS 25-0390).

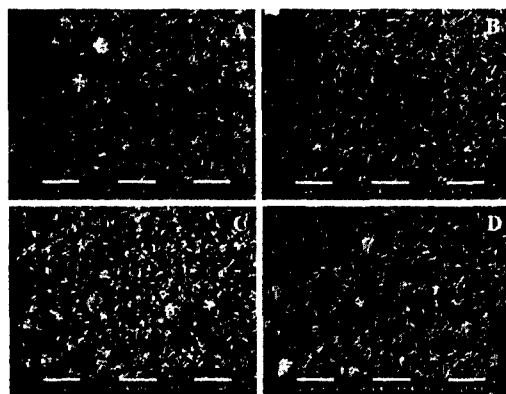


Figure 2. Scanning electron micrographs of In_2S_3 thin films deposited from baths containing InCl_3 , thioacetamide and carboxylic acid; *a.* citric (pH = 1.95); *b.* formic (pH = 2.2); *c.* succinic (pH = 2.3); *d.* acetic (pH = 2.1).

Scanning Electronic Microscopy

The effect of different carboxylic acids on CBD- In_2S_3 film morphology was probed by scanning electron microscopy (SEM). For all systems under investigation (within the optimal pH range), films were composed of dense, ribbon-like primary crystallites (Figure 2). The smallest crystallites were obtained from baths containing citric acid, which has the lowest $\text{pK}_{\text{a}1}$. Films formed from baths containing acetic or citric acid were morphologically similar and composed of spheroidal aggregates comprising primary ribbon-like crystallites. These clusters appeared to follow the underlying TO layer. The most homogeneous films, which did not conform to the underlying TO layer, were deposited from baths containing formic acid. Films deposited from baths containing succinic acid were less ordered than all others in this study

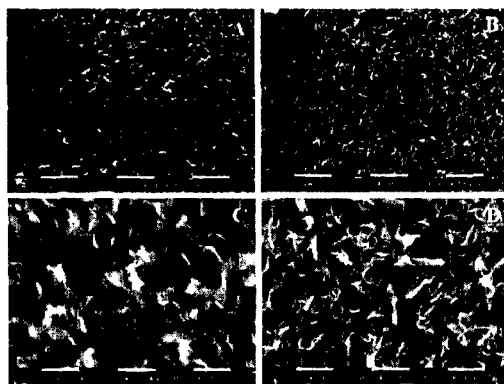


Figure 3. Scanning electron micrographs of In_2S_3 thin films deposited from baths containing InCl_3 , formic acid and thioacetamide at pH values of 2.2 (top); *a.* as deposited; *b.* annealed and 1.4 (bottom); *c.* as deposited; *d.* annealed

In order to complement the results obtained from XRD studies for films deposited from baths containing formic acid, the effect of annealing and CBD solution pH on In_2S_3 film morphology were investigated. As seen clearly in Figure 3, the pH of the deposition bath has a pronounced effect on film morphology. Films deposited at pH values lower than the optimal range (*i.e.* matt films) were composed of flaky aggregates, as opposed to the specular films obtained in the optimal pH range. Annealing of these flaky films produced pronounced changes and an improvement in crystallinity. By contrast, no significant changes in morphology were apparent upon annealing of specular films.

XPS

XPS was employed to determine photoelectron binding energies of components of annealed films. As shown in Figure 4 (left), In, S, O and C were detected. The O 1s peak, located at 533 eV, was ascribed to molecular oxygen contamination from the ambient on the basis of previous literature reports [10]. The absence of an additional peak at 530 eV was taken as evidence that oxygen was not bonded to the metal [10], although Herrero *et al.* assign this peak to C-O/H₂O [9]. No evidence for the formation of an In-O-S alloy was obtained. For example, the In Auger parameter corresponding to In_2S_3 and $\text{In}(\text{OH})_3$ is known to occur at 852.2 eV and 850.8 eV [11], whereas the feature occurs at 853 eV in our spectrum. In addition, Hariskos *et al.* state that the occurrence of an alloy results in attenuation of the feature at 404.5 eV due to an Auger contribution from In (MNN) electrons of $\text{In}(\text{OH})_3$. Expansion of the aforementioned region in our spectrum revealed no such phenomenon. Incorporation of oxy-sulfide species was discounted, as the S 2p peak binding energy (161 eV) is lower than would be expected for S-O bonds (~ 168 eV) [10]. The most significant feature of the spectrum, with a binding energy of 444.5 eV, was assigned to $\text{In}3d_{5/2}$ photoelectrons. The feature is consistent with literature values for In_2S_3 [12].

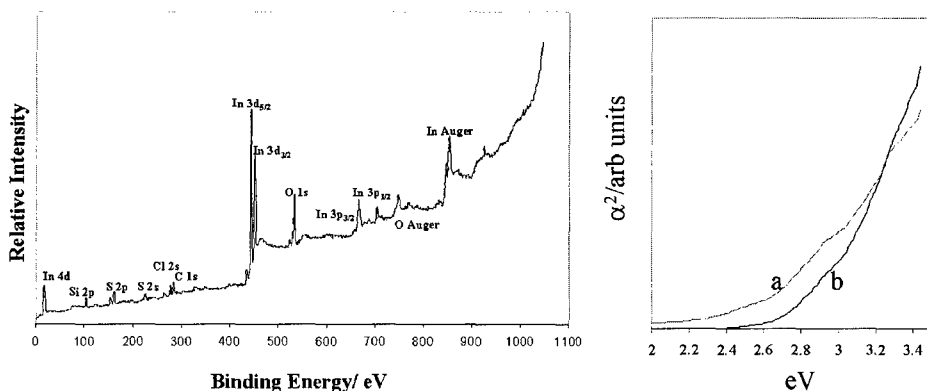


Figure 4. X-ray photoelectron (left) and electronic absorption spectra (right) of In_2S_3 thin films deposited from baths containing InCl_3 , acetic acid and thioacetamide; a. annealed, b. as-deposited (right.)

Electronic Spectroscopy

Electronic absorption spectra of as-deposited and annealed In_2S_3 films were recorded. From the extrapolation of the linear region of plots of α^2 versus $h\nu$ (eV), the bandgaps were determined. Annealed films possessed bandgaps of 2.58 eV (Figure 4, right), slightly lower than those of as-deposited films (2.78 eV). The result was very similar to values reported by Lokhande *et al* [6]. The most rational explanation for the increased bandgap values is the manifestation of quantum-size effects; the visible colour change upon annealing (*i.e.* yellow to pale orange) is also consistent with this interpretation.

CONCLUSIONS

The reproducible CBD of $\beta\text{-In}_2\text{S}_3$ thin films on TO-glass substrates has been demonstrated. Baths containing carboxylic acids yield adherent and crystalline films within a defined pH range, which is dependent on the particular acid employed.

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